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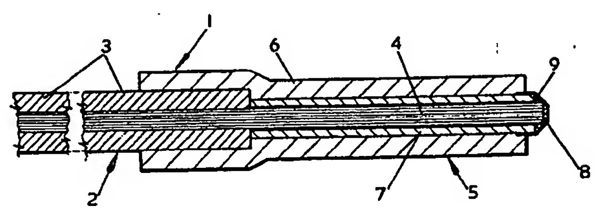
(54) **Optical fibre probe.**

(57) A probe 1 comprises a sensor portion 5 having an outer porous hydrophobic membrane 8 (e.g. PTFE) and, within the sensor portion 5, a material 9 comprised of a hydrophobic resin (e.g. cross-linked polystyrene) on which is immobilised a compound having spectral characteristics sensitive to a change to be monitored by the probe. Optical fibre cable 2 transmits light from a source to the compound and back to a detector. A change in the parameter being monitored by the probe results in a spectral change in the compound which is detected by the detector.



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OPTICAL FIBRE PROBE

This invention relates to a probe for monitoring a change in a parameter of interest, e.g. a chemical parameter such as the nature or concentration of a chemical species in solution or in the gaseous phase.

Various types of electrical probes are already known. These probes do however have a number of disadvantages. Firstly, the probes rely on the use of electrical signals which may be undesirable if the probe is to be used in an inflammable environment. Secondly, there may be impedance effects in the electrical probe which adversely affect the measurement being made. The problems associated with impedance effects become particularly acute when miniturarised probes are required. In this case, it may be necessary to operate the probe within a Faraday cage to avoid the impedance effects.

It is an object of this invention to provide a probe which obviates or mitigates the above disadvantages.

According to the present invention there is provided a probe comprising a sensor portion having an outer porous hydrophobic membrane and, within the sensor portion, a hydrophobic resin on which is immobilised a compound having spectral characteristics sensitive to a change to be monitored by the probe, and optical fibre means for transmitting light to said compound and for transmitting light from said compound to d tect any spectral change therein.

In use, the probe of the invention is associated with light source and a light detector. Light from the source is transmitted along the optical fibre to the compound (herein referred to as the indicator compound) having spectral characteristics sensitive to a change to be monitored and back from the indicator compound to the detector. The detector may be set to detect the intensity of light returned from the indicator compound at a wavelength at which the intensity will alter when the spectral characteristics of the indicator compound change due to a change in the system under investigation.

The use of hydrophobic porous membranes and hydrophobic resins are important features of the invention as the hydrophobicity of these materials ensures that interactions between the components of the analyte phase, except the analyte species itself, and all parts of th probe except for the indicating compound or formulation are minimised.

The porous membrane serves to retain the resin and indicator compound in position and allows any chemical species under investigation to diffuse through to the indicator compound whilst inhibiting the diffusion of undesired particulate matter. Also for vapour phase or gaseous state determinations where the indicator compounds may requir some d gr e of hydration and the membrane can serve to retain moisture by virtu of its hydrophobicity.

PTFE (polytetrafluoro thylene) is the pref rred

material for the porous hydrophobic membrane.

The hydrophobic resin which serves to support and retain the indicator compound is preferably a cross-linked polystyrene, particularly a cross-linked polystyrene without any chemically active groups. Polystyrene resins cross-linked with divinyl benzene may be used as the resin. Suitable resins are the XAD resins (produced by Rohm and Haas). Resins supplied in granular form are preferably ground before use in the probe. The use of powders enhances the diffuse reflection or emission characteristics at the interface between the optical fibres and the resin (see below) and also allows the construction of smaller probes.

The indicator compound is adsorbed on the retained by the hydrophobic resin, i.e. the resin immobilises the indicator compound. This indicator compound is at least one reagent which undergoes a change in spectral characteristics in response to a change in the parameter under investigation, e.g. a change in the nature or concentration of a particular chemical species investigation. The spectroscopic change may be one of phosphorescence, fluorescence or simply colour change depending on the reagent used. Suitable indicator compounds are colorimetric indicator dyestuffs selected having regard to the change which the probe is to monitor. Bromothymol Blue is one example of such a colorimetric dyestuff. Bromothymol Blue is

yellow in acid solution and blue in alkaline solution and may thus be used in a probe intended for monitoring pH changes.

The transmissive and receptive optical fibre means may be a single fibre or bundle of fibres arranged in ordered or random fashion. The use of a single fibre does however require complex instrumentation to separate the source light signal from the returning light signal. In practice, it is more convenient to use a bundle of fibres which is split such that one half is connected to the light source and the other to the detector.

The interface between the optical fibre means and the resin with immobilised indicator compound may tak the form of a direct and intimate contact or the optical fibres may be maintained at a discrete distance from the resin by an inert transparent medium preferably indexed matched to the core material of the fibre.

The invention will be further described by way of example only with reference to the accompanying drawing which shows a sectional view of the sensor of one embodiment of probe in accordance with the invention

The illustrated probe 1 comprises an optical fibre cabl 2 (including sheathing 3 and a plurality of individual fibr s 4) and a sensor 5 formed as a tip for the probe 1. The sensor 5 itself comprises an outer

plastics tube 6, one end of which is fitted over the end of the sheathing 3 of the cable 2, and an inner guide tube 7 one end of which abuts against sheathing 3 and the other end of which projects beyond tube 6. Provided across the end of tube 7 is a porous PTFE membrane 8. Between the end of tube 7 and the membrane 8 is a material 9 formed of a cross-linked powdered polystyrene having immobilised thereon a reagent giving a spectroscopic change in response to a change in the parameter to be investigated. The material 9 is, as will be seen from the drawing, located beyond the end of tube 7.

As illustrated in Fig. 1, the optical fibres 4 are in intimate contact with the material 9. At their ends remote from the sensor 5, one half of the optical fibres 4 are connected to a light source (not shown) and the other half are connected to a detector (not shown). The distance of the light source and detector from the sensor 5 may be limited only be optical losses in the cable 2 so that the sensor 5 may at some distance remote from the light source and detector.

To give an idea of size, the sensor 5 of the illustrated probe 1 may be of a length of about 10mm whereas the optical fibre cable may have a diameter of about 2mm. These dimensions are given purely by way of example, and may of course be different to suit particular applications for the probe 1. Particularly, miniaturisation of the sensor would allow use of the

sensor would allow use of the prob in clinical and other biomedical applications.

The illustrated probe is particularly useful as a pH sensor although it does have many other applications.

For use as a pH sensor, the indicator compound may be Bromothymol Blue which as mentioned above is yellow in acid and blue in alkali. In operation, the sensor 5 is positioned in a solution of which the pH is to be investigated. The light source used is one emitting red light at a wavelength of 635 nanometers and the detector measures the intensity of light returned from the sensor at this wavelength. When the solution under investigation is alkaline, the Bromothymol reagent is blue and absorbs a high proporation of the incident red light. When the solution becomes acidic, the Bromothymol reagent becom s yellow and reflects a high proportion of the incident red lgiht which is then retransmitted <u>via</u> the fibre to the detector. This change in the spectral characteristics of the Bromothymol reagent is detected by the detector which thus indicates that the solution has undergone a pH change from alkaline to acid. It should at this point be noted that hydrogen ion diffusion through the membrane 8 is rapid, and this is believed to be due to the fact that membrane 8 projects beyond the end of tube 7.

The probe may thus be used simply to indicate a change of pH b tween alkalinity and acidity. Alternatively the prob may previously have been calibrated so that the extent of th change in intensity

of the detected wavelength gives a quantitative indication of the pH change.

The probe of the invention has a number of significant advantages.

Firstly, the probe is of robust construction and this is advantageous particularly for pH measurements as the use of fragile glass electrodes is avoided. Coupled with this, the flexibility of the optical fibres allows the probe to be used in locations which would be inaccessible with rigid glass electrodes.

Secondly, the sensor of the probe may be positioned in a hazardous (e.g. inflammable) environment whereas the electrical instrumentation for the probe (i.e. light source, detector) may be remote from the probe outside of the hazardous environment. The probe is intrinsically safe in inflammable environments as no electrical signals pass to the remote instrumentation.

Thirdly, there are no adverse impendance effects resulting from the small size of the probe as might be the case for miniaturised electrical probes.

CLAIMS:

1. A probe comprising a sensor portion having an outer porous hydrophobic membrane and, within the sensor portion, a hydrophobic resin on which is immobilised a compound having spectral characteristics sensitive to a change to be monitored by the probe, and optical fibre means for transmitting light to said compound and for transmitting light from said compound and for transmitting light from said compound to detect any spectral change therein.

2. A probe as claimed in claim 1 wherein the sensor is provided as a tip for the probe.

3. A probe as claimed in claim 2 wherein the porous membrane forms a projection at the end of the tip.

4. A probe as claimed in any one of claims 1 to 3 wherein the optical fibre means are in intimate contact with the resin and immobilised compound.

5. A probe as claimed in any one of claims 1 to 4 wherein the membrane is of polytetrafluoroethylene.

6. A probe as claimed in any one of claims 1 to 5 wherein the resin is used in powdered form.

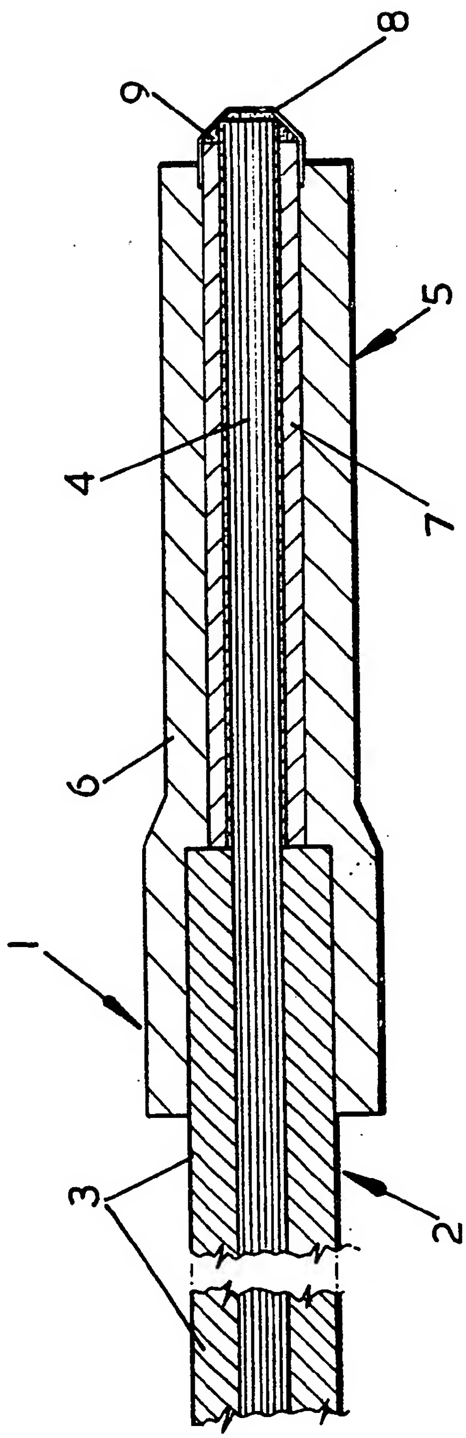
7. A probe as claimed in any one of claims 1 to 6 wherein the hydrophobic resin is a cross-linked polystyrene.

8. A probe as claimed in claim 7 wherein the resin has substantially no chemically active functional groups.

9. A probe as claimed in claim 7 or 8 wherein the polystyrene is cross-linked with divinyl benzene.

10. A probe as claimed in any one of claims 1 to 9 wherein the immobilised compound is a colorimetric reagent.

11. A probe as claimed in claim 10 wherein the immobilised compound is Bromothymol Blue.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